CHINA SCHOLARSHIP COUNCIL

Appel à projets
Campagne 2022
https://www.sorbonne-universite.fr

Title of the research project :

Pseudo-Chiral and achiral nanostructures to boost the detection of chiral biomolecules

Thesis supervisor (HDR) :

Name : Gallas Surname : Bruno

Title : CR

email : bruno.gallas@insp.jussieu.fr

Professional adress :
(site, dresse, bulding, office…) campus Jussieu, tour 22-32-523

Research Unit

Name : Institut des NanoSciences de Paris

Code *(ex. UMR xxxx)* :

UMR 7588

Doctorate School

Thesis supervisor's doctorate school (candidate's futur doctoral school) : ED 397

PhD student currently supervised by the thesis supervisor (number, year of the first inscription) :

3rd year (joint with S. Boujday) ; 1st year (joint with M. Mivelle)

SORBONNE UNIVERSITÉ

Joint supervisor :

Name : Souhir   Surname : Boujday

Title : Pr

email : souhir.boujday@sorbonne-universite.fr

Professional adress :
(site, dresse, bulding, office…)
Campus Jussieu, tour 33-43-322

Research Unit

Name : Laboratoire de Réactivité de Surface

Code *(ex. UMR xxxx)* :
UMR 7197

École doctorale

Joint supervisor's doctorate school :   Or, if non SU :
ED 397

PhD student currently supervised by the joint supervisor (number, year of the first inscription) :
3rd year (joint with B. Gallas) ; 2nd year (CSC, joint swith M. Salmain) ; 1st year (m

----

Joint supervisor :

Name :   Surname :

Title :

email :

Professional adress :
(site, dresse, bulding, office…)

Research Unit

Name :

Code *(ex. UMR xxxx)* :

École doctorale

Joint supervisor's doctorate school :   Or, if non SU :

PhD student currently supervised by the joint supervisor (number, year of the first inscription) :

SORBONNE UNIVERSITÉ

CHINA SCHOLARSHIP COUNCIL

Pseudo-Chiral and achiral nanostructures to boost the detection of chiral biomolecules

The detection of molecules based on fluorescence or Raman scattering has been widely studied and is currently used in industry and laboratories. However, many organic molecules of interest are chiral, and their chemical and biological properties depend on their enantiomer as well as on the chirality of their secondary structure. The quantity and chirality of biomolecules are classically determined by measuring the differential absorption between the two opposite circular polarizations (chiroptic method). However, this method is limited by the low differential absorption of chiral molecules, which is of the order of 10^{-3} in the UV part of the spectrum. Plasmonic resonators have the ability to resonantly interact with light and are characterized by a moderate quality factor and a low effective volume. This resonant interaction allows (i) to increase the coupling between molecules and light and (ii) to control the polarization properties of light. In this PhD project we propose to use plasmonic nanoresonators to increase the light -"chiral matter" interactions in order to detect and study chiral molecules. The presence of a molecule in close proximity of a plasmonic nanoresonator induces a modification of the electromagnetic environment around the photonic nanoresonator, resulting in a shift of its resonant scattering spectrum [1] and in its polarization properties [2,3]. So far, the latest advances concern the implementation of nanostructured chiral surfaces with gammadion-type resonators [4-6] or stacked twisted resonators [7] that interact preferentially with a given helicity of light. However, **the mechanism behind the differential response of biomolecules coupled to chiral resonators to circularly polarized light is still unclear**, preventing the optimization of such detection. Moreover, in the research published so far, two different chiral sensors are needed to interact with right- and left-handed circularly polarized light, which requires complex calibration procedures. We propose to use anisotropic achiral nanostructures to interact with chiral molecules. Indeed, they have a significant advantage over chiral nanostructures of changing the sign of the circular dichroism by controlling the incident linear polarized or the direction of propagation [8,9].

The symmetries of the electromagnetic field in close proximity to the resonators can be manipulated at will by changing illumination conditions hence providing a unique tool for studying the origin of the electromagnetic coupling between chiral biomolecule and nanoresonators. The objective of this project is to develop the detection of chiral molecules coupled to optical nanoantennas. **In this work, we will use the concept of achiral plasmonic nanostructures to develop innovative nanoresonators that will be used, once functionalized, to detect chiral biomolecules with enantiomer sensitivity.** At first, the biomolecule that we will be considered will be light-harvesting complexes (LH2) extracted from photosynthetic bacteria. These are chiral molecules that have been selected throughout evolution to harvest the energy of light extremely efficiently, which make them very interesting for photovoltaic technologies for instance. They present a strong absorption band in the red part of the visible spectrum exhibiting circular dichroism which make them ideal probes to study the electromagnetic coupling of chiral molecule to plasmonic resonators. We will then develop the detection of proteins of medical interest such as β-lactoglobulin (allergen) or immunoglobulin G which is an antibody that helps the human body fighting infectious diseases…

The PhD project will be developed in a collaborative framework using the expertise of two Laboratories of Sorbonne University located on the same campus : The Institut des NanoSciences de Paris (INSP) with B. GALLAS as joint supervisor and the Laboratoire de Réactivité de Surface (LRS) with S. BOUJDAY as joint supervisor. Although this project is self-contained, the applicant will have the opportunity to interact closely with scientist and the other PhD students of our groups. This project can be divided in 3 Tasks that interact closely among each other.

Task 1: Fabrication and optimization of photonic nano-antenna.

The first task of this proposal will be devoted to the design, simulation and fabrication of the photonic antennas. The first objective is to simulate the full plasmonic response of the photonic antenna to design the optimal structure able to manipulate, in the near field, the symmetries of the electromagnetic fields.

This is a key point since according to the local behavior of this field, the antenna will couple either to one chirality of the molecule or the other (Fig. 1a). For that purpose, finite difference time domain (FDTD) method will be used (Lumerical). The antennae will be then fabricated on 2D substrates by electron lithography in the clean room of the INSP (Fig. 1b).

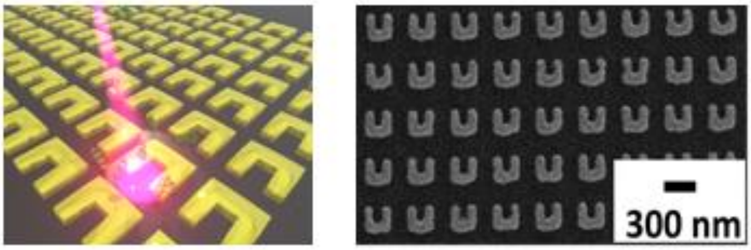

Fig. 1: (a) modelization of the interaction of nanoresonators with light and chiral molecules. (b) Scanning Electron Microscopy image of a surface containing U-shaped resonators realized by e-beam lithography at the INSP.

Task 2: Surface functionalization

The molecules need to be in the close vicinity of the photonic resonators so that the near-field can probe them. It is quite rare that these conditions are met naturally and functionalization of the resonators surface is mandatory. In addition, in a detection perspective, surface functionalization may become necessary to obtain a specific absorption and to master the mechanism and amount of adsorbed molecules. The surface functionalization will be performed at the LRS which has been developing successfully plasmonic sensing for many years now.

Task 3: Optical reporting of the chirality of the molecules.

The detection of the chirality of the molecules is based on polarimetric measurements. This task will use in a first step the generalized ellipsometric setup already present at the INSP. This setup allows for the full polarimetric measurement of the surface containing the nanoresonators upon molecule absorption. The current setup has been adapted for doing measurements in liquid environment (Fig. 2a) which allows real time monitoring the polarimetric response of the surface upon absorption of molecules (Fig. 2b).

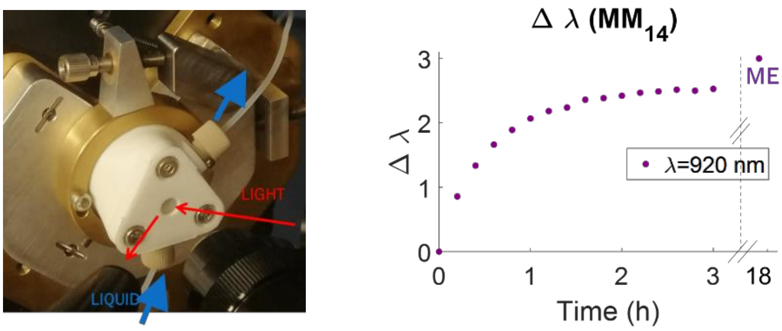

Fig. 2: (a) liquid cell for the measurement of polarimetric properties in liquid environment. (b) Temporal evolution of the spectral position of a plasmonic band characterized by a strong circular dichroism originating in Magneto-Electric (ME) coupling upon absorption of an anti-bacterial peptide.

The objectives of this project are to extend the current measurements to the LHII proteins. These proteins present characteristic dichroic absorption bands in the near infrared. It will then possible to match the plasmon resonances of the photonic nanostructures with the characteristic bands of the light harvesting proteins (Task. 1) allowing for a full control of the light-matter interaction.
Once the best detection measurements being determined (Tasks 1) we want to develop a new detection setup based on an optical microscope allowing for full polarimetric measurements in reflection in the Fourier plane. The objective is measuring in one acquisition step the polarimetric properties for all possible propagation directions. A setup has been recently been developed at the INSP in transmission

configuration [10] and must be adapted for reflection measurements, hence allowing measurements in liquid environment (Fig 3).

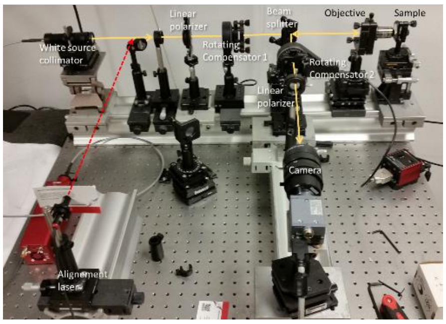

Fig 3: photograph of the micropolarimeter being mounted in reflection configuration

Project Impacts : **Developing new photonic structures to specifically enhance the coupling between light and chiral molecules is a new and exciting field of research.** Understanding how light interacts with chiral matter down to the nanometer level will open new paradigms in technologies as well as in applied and fundamental science. *For nanophotonics:* By manipulating electromagnetic field symmetries at the nanoscale, new and exotic behaviors such as nanosources of exotic polarizations will become possible. *For photovoltaic technologies:* Light-harvesting complexes have developed, through evolution, extremely efficient mechanism to harvest the energy of light. Understanding the mechanism of chiral light absorption will bring us closer to replicate this extraordinary property. *For medical science:* The antibacterial reactivity of some peptides relies on their chirality which can be affected by their absorption onto a surface. This behavior is not yet fully understood but holds huge promises, for instance for surgical tools. *For ultra-sensitive sensing:* the possibility to detect single chiral molecules would be extremely useful in biological and sensing science since most of our proteins are chiral. Although many fantastic applications are envisioned based on "nanochiral light" and chiral matter interactions, experimental works are still scarse. It is, therefore, of great importance to experimentally understand this field in order to develop applications and technologies.

References

[1] Rotello, G. Cooke, A. Lapthorn, M. Kadodwala, "Superchiral" Spectroscopy: Detection of Protein Higher Order Hierarchical Structure with Chiral Plasmonic Nanostructures," J. Am. Chem. Soc. **137**, 8380−8383 (2015)
[2] M. Nesterov, X. Yin, M. Schäferling, H. Giessen, T. Weiss, ACS Photonics **3**, 578 (2016)
[3] J. Slocik, A. O. Govorov, R. R. Naik, Nano Lett. **11**, 701 2011
[4] C. Jack, A.S. Karimullah, R. Leyman, R. Tullius, Vi.M. Rotello, G. Cooke, N. Gadegaard, L.D. Barron, and M. Kadodwala, "Biomacromolecular Stereostructure Mediates Mode Hybridization in Chiral Plasmonic Nanostructures", Nano Lett. **16**, 5806– 5814 (2016)
[5] E. Hendry, T. Carpy, J. Johnston, M. Popland, R. V. Mikhaylovskiy, A. J. Lapthorn, S. M. Kelly, L. D. Barron, N. Gadegaard and M. Kadodwala, "Ultrasensitive detection and characterization of biomolecules using superchiral fields", Nature Nanotech. **5**, 783-785 (2010)
[6] C. Jack, A. S. Karimullah, R. Tullius, L. K. Khorashad, M. Rodier, B. Fitzpatrick, L. D. Barron, N. Gadegaard, A. J. Lapthorn, V. M. Rotello, G. Cooke, A.O. Govorov & M. Kadodwala, "Spatial control of chemical processes on nanostructures through nano-localized water heating" Nature Commun. **7**, 10946 (2016)
[7] Y. Zhao, A.N. Askarpour, L. Sun, J. Shi, X. Li & A. Alu, "Chirality detection of enantiomers using twisted optical metamaterials" , Nat. Comm. **14180**, 1 (2017)
[8] Julien Proust, Johan Grand, Nicolas Bonod, Bruno Gallas, ACS Photonics **3**, 1581-1588 (2016)
[9] T. Sang Hyuk Yoo, J. Berthelot, G. Guida, D. Demaille, E. Garcia-Caurel, N. Bonod, B. Gallas, ACS Photonics **5**, 4068-4073 (2018)
[10] M. Nicolas, I. Soumahoro, L. Zhang, G. Guida, W. Daney de Marcillac, D. Demaille, C. Schwob, S. Boujday, B. Gallas, J. Opt. Soc. Am. B **38**, 1184-1191 (2021)